(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 073 174
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 82630083.2

(22) Date of filing: 20.08.82

(51) Int. Cl.³: C 08 J 5/10
C 08 L 21/00

(30) Priority. 25.08.81 US 296027

(43) Date of publication of application:
02.03.83 Bulletin 83/9

(84) Designated Contracting States:
DE FR GB

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(54) Composite of rubber and metal reinforcement therefor.

(57) Composite of rubber composition and filament reinforcement therefor where said rubber composition contains certain selected components for the purpose of enhancing rubber adhesion to said filament. The composite can be used in various articles of manufacture such as tires and industrial products.

EP 0 073 174 A1

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TITLE: COMPOSITE OF RUBBER AND METAL REINFORCEMENT THEREFOR

Field of Invention

This invention relates to the adhesion of metal and/or alternately, organic or inorganic fibers, to elastomers. The invention particularly relates to a composite of rubber and wire filament or cabled filaments in the form of a cord or fiber as reinforcement therefor. The invention further relates to a composite of sulfur cured rubber and tire cord, composed of at least one metallic-plated steel filament as a reinforcement therefore, and particularly to a pneumatic or semi-pneumatic rubber tire containing such reinforcement. The invention additionally relates to rubber industrial power transmission belts, conveyor belts and to rubber hose containing such reinforcement.

Background of the Invention

Adhesion of rubber to metal or organic or inorganic fibers has, for a long time, been the subject of considerable experimentation and research. Various solutions have been suggested and have provided various degrees of success.

For example, various physical configurations of cables wire filaments have been used to enhance physical or mechanical adhesion to rubber. Also, the surface of wire filaments has been treated by various materials and methods to enhance adhesion to rubber. Further various materials have been mixed with the rubber itself in an effort to increase its adhesion to a cord of cabled wire filaments or organic fiber filaments.

In one aspect, boric acid, orthoboric acid, lead borate, sodium borate, and cobalt borate have been taught to be useful for aiding in the bonding of rubber to brass, bronze, iron, aluminum, and titanium. For example, see British Patent No. 1,338,930. Also, certain triazine compounds

(GE DT - 2,318,283 and U.S. Patent 3,517,722) and benzoic or hydroxy benzoic acids (GE Patent DT 2,527,574) have been taught or suggested for bonding rubber to steel or copper alloys.

Such rubber-metal reinforced composites are often applicable to the construction of pneumatic tires, industrial belts and hose.

However, even with the extensive amount of work and suggested solutions, methods of enhancing adhesion of rubber to metal or, alternately, organic and inorganic fibers are still being sought.

Disclosure and Practice of the Invention

In accordance with this invention, a composite of sulfur-vulcanized rubber composition containing zinc oxide, carbon black, optionally and/or mineral fillers such as clay and/or precipitated silica, cure accelerators, fatty acid and/or ester thereof such as stearic acid or zinc stearate and filament reinforcement therefor is provided selected from at least one of metal, organic and inorganic filaments, preferable metal filament, where said metal reinforcement is at least one cord of at least one metallic-plated steel wire filament adhered to said rubber at least in part through sulfur vulcanization, characterized in that said rubber composition contains (A) from about 0.1 to about 10 preferable about 0.2 to about 5 parts by weight per 100 parts by weight rubber (phr) compound selected from diallyl phthalate, diallyl isophthalate and low molecular weight homopolymer thereof, diallyl terephthalate, diallyl itaconate, N,N'-diallyl tartardiamide, N.N'-diallyl melamine, diallyl adipate, diallyl succinate, diallyl sebacate, diallyl oxalate, diallyl maleate, diallyl azelate, triallyl trimellitate, triallyl citrate, and triallyl orthoformate, triallyl borate, trimethylol propane trimethacrylate, divinyl benzene and diallyl malonate.

In the practice of this invention, the following compounds are preferred: diallyl phthalate, diallyl isophthalate and low molecular weight homopolymers thereof, diallyl terephthalate, diallyl itaconate, triallyl orthoformate, triallyl trimellitate and triallyl citrate.

In further accordance with this invention, such a composite is provided of the sulfur-vulcanized rubber composition and, containing therein as reinforcement therefor, at least one filament selected from at least one of metal, organic and inorganic, preferably metal filaments, optionally as a multiple of filaments cabled together as a cord, where said metal filament is composed of a steel filament having a microscopically thin metallic coating thereon comprised primarily of brass and/or zinc.

It is appreciated that such metallic-coated steel filament can optionally also have a thin overcoat thereon of protective compound such as, for example, benzotriazole or similarly protective compound.

In further accordance with this invention, a pneumatic and/or semi-pneumatic rubber tire is provided typically having a generally toroidal shape and comprised of a general construction containing a tread, spaced inextensible beads and sidewalls connecting said beads and tread and with a supporting carcass therefor, where said carcass is a metal filament-reinforced sulfur-cured rubber composite of this invention.

In addition, in accordance with this invention, an industrial article of manufacture is provided selected from at least one of industrial conveyor belt, power transmission belt and hose which are, at least in part, constructed of the metal filament-reinforced sulfur-vulcanized rubber composite of this invention.

It is understood that other conventional materials can be used in the compounding of the rubber which include

antidegradants, tackifying resins of the non-reactive type, peptizers, fillers and/or pigments and processing oils. Although it is related herein that the various mineral fillers can be used, usually the carbon black is preferred.

For the compounding of the rubber and the preparation of the wire/rubber composite, the compounding materials are simply mixed together to form the compounded rubber and applied to the filament or cord thereof, usually in a form of a textile type fabric form, such as by calendering and the resulting composite built into a green tire, industrial belt or hose construction and the product simply molded and cured with the aid of pressure to form the article of manufacture. Generally, the rubber/metal composite is cured at a temperature in the range of about 50°C. to about 200°C.

Various rubbers can be used in the practice of this invention of which unsaturated types are preferred. Representative of such unsaturated rubbers are, for example, at least one of natural rubber, synthetic cis-1,4-polyisoprene, polychloroprene, cyclene rubbers, rubbery polymers of 1,3-butadiene, butadiene/styrene copolymers, isoprene/styrene copolymers, epichlorohydrin homo and copolymers with alkylene oxides isoprene/α-methylstyrene copolymers, butadiene/acrylonitrile copolymers, EPDM rubbers, butyl rubbers, halobutyl rubbers, norbornene rubbers, thiokol rubbers and blends thereof with a minor portion of rubbery block copolymers selected from at least one of styrene/isoprene/styrene and styrene/butadiene/styrene block copolymers.

The wire cord itself in the practice of this invention can be composed of 1 to 50 (or more) filaments of steel wire twisted, or cabled together to form the cord. Therefore, the cord can be monofilament in nature although this is considered rare and at least four filaments are usually preferred. For example, for use in pneumatic rubber tires, cord for passenger tires might be composed

of 3 to 6 cabled filaments, cord for truck tires 10 to 30 cabled filaments and cord for giant earthmover vehicle tires 40 to 50 cabled filaments.

It is generally preferred that the steel filaments themselves are individually coated, or plated, with transition metal or alloy thereof which are preferably microporous, often practically monomolecular representative of which are at least one of those selected from brass, zirconium, cerium, lanthanum, nickel, cobalt, tin, titanium, zinc, copper and bronze. Generally, an outer monomolecular, microporous layer of zinc is suitable over a very thin brass plate on the steel wire.

It is recognized that the steel wire can be plated or coated with the metal or metal alloy such as brass and/or transition metal or alloy by various methods to obtain a thin, preferably a practically monomolecular coat and usually somewhat microporous in nature. For example, electro deposition can be effected by passing the wire through a charged electrolyte bath.

It may also be feasible to use a vapor deposition technique to plate the wire.

The metal coating on the steel is generally microscopically porous, thereby understood to expose small areas of steel surface.

It is not reasonably practical to describe within rigid limits the metal plating on the steel wire. Optimum thicknesses and amounts can be a function of variables such as nature of the brass, zinc, or brass-zinc or metal alloy surface, mode of deposition, thickness of initial oxide layers, magnitude of residual stresses, copper content, brass thickness, as well as the reactivity of the rubber vulcanization system.

The steel wire can relate generally to what is known as carbon steel, also called ordinary steel, also called straight carbon steel or plain carbon steel, e.g., American Iron and Steel Institute Grade 1070 high carbon steel (AISI 1070). Such steel owes its properties chiefly

to the presence of carbon without substantial amounts of other alloying elements. In this respect see Metals Handbook, The American Society for Metals, Metals Park.

Brass generally and preferably relates to compositions in which the major component is alpha brass, i.e., which contain from about 62 to 75 percent copper and 38 to 25 percent zinc, respectively.

The cross-linkable monomer can be mixed with the rubber and its compounding ingredients by conventional procedures prior to application to the metal filament (wire) or organic or inorganic fibers.

As hereinbefore pointed out, the plated wire may contain a coating of protective material such as benzotriazole and the like prior to application of the compounded rubber. Such protective agent coatings are those which are believed to somewhat interact with copper in a brass coating on the steel wire to form a polymeric complex of agent plus copper and/or zinc. This polymeric complex is insoluble in most solvents and serves as a protective barrier to environmental degradation of the underlying brass.

The practice of the present invention has been observed to result in improved aged rubber-metal adhesion, in many cases with improved initial, i.e., original adhesion of vulcanized brass-coated steel/rubber composites.

The practice of this invention is further illustrated by reference to the following example which is intended to be representative rather than restrictive of the scope of the invention. Unless otherwise indicated, all parts and percentages are by weight.

Example I

A compounded rubber was prepared as a control by mixing cis-1,4-polyisoprene rubber with various compounding ingredients which included the materials shown in the following Table 1 and the compound (compounded rubber) identified herein as Control X.

Table 1

Composition (PHR)	Control X	Control Y
Polyisoprene Rubber	100	100
Stearic Acid	2.0	-
Oleic Acid	-	2.0
Zinc Oxide	8.0	8.0
Antidegradants	0.75	1.5
Carbon Black	60.0	65.0
Tackifying Resin and Processing Oil	4.0	3.5
Resorcinol and Hexamethoxy Methyl Melamine	4.0	4.0
Sulfur	4.0	5.2
Accelerator, sulfenamide-type	1.0	0.65
Cobalt salt of organic acid (10-11%Co)	3.0	1.75
Retarder	0.2	-

The recipe for the Control X compounded rubber was modified as shown in Tables 2, 3 and 4 and compounded rubber samples prepared thereby in experiments identified herein as experiments or Example A in Table 2, Examples B-G in Table 3, and Examples H-J in Table 4. The recipe for Control Y was modified as shown in Table 5 with Examples K-N.

Table 2

Compounds added to Control X Recipe	Control X	A
Diallyl Phthalate	-	1.8
Adhesion (SBAT)		
Pullout Force in Lbs		
i) Original Adhesion	263	267
ii) Humid Aged (10 days/ 77°C/98% RH)	154	187
iii) Salt Aged (5% NaCl/H_2O/ 48 hrs/90°C)	160	240
iv) Oven Aged (7 days/N_2/ 121°C)	190	202

Table 3

Composition (PHR)	Control X	B	C	D	E	F	G
Diallyl Isophthalate	-	0.75	-	-	-	-	-
Diallyl Isophthalate Homopolymer, low molecular weight	-	-	1.0	-	-	-	-
Diallyl Terephthalate	-	-	-	1.0	-	-	-
Diallyl Itaconate	-	-	-	-	1.0	-	-
N,N'-Diallyl Tartardiamide	-	-	-	-	-	1.0	-
N,N'-Diallyl Melamine	-	-	-	-	-	-	0.6
Adhesion (TCAT, Pullout Force in Newtons)							
i) Original Adhesion:	574	582	597	589	615	614	609
ii) Aged Adhesion (10 days/H_2O/90°C)	429	566	500	583	663	494	443

Table 4

Composition (PHR)	Control X	H	I	J
Triallyl Orthoformate	-	1.0	-	-
Triallyl Trimellitate	-	-	1.0	-
Triallyl Citrate	-	-	-	1.0
Adhesion (TCAT, Pullout Force in Newtons)				
i) Original Adhesion	574	544	551	576
ii) Aged Adhesion (10 days/H_2O/90°C)	429	618	592	610

Table 5

Composition (PHR)	Control Y	K	L	M	N
Triallyl Orthoformate	-	1.0	-	-	-
Triallyl Trimellitate	-	-	1.0	-	-
Triallyl Citrate	-	-	-	1.0	-
Diallyl Terephthalate	-	-	-	-	1.0
Adhesion (TCAT, Pullout Force in Newtons)					
i) Original Adhesion	549	542	551	526	540
ii) Aged Adhesion (10 days/ H_2O/90°C)	255	532	268	487	335

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes and modifications may be made therein without departing from the spirit of scope of the invention.

WHAT IS CLAIMED IS:

1. A composite of rubber composition containing zinc oxide, carbon black, optionally and/or mineral fillers, cure accelerator(s), fatty acid and/or metal salt thereof, and filament reinforcement therefor where said filament is selected from at least one of metal, organic and inorganic filaments, optionally as a multiple of filaments cabled together to form a cord characterized in that said rubber composition contains about 0.1 to about 10 parts by weight per 100 parts by weight rubber (phr) a compound selected from at least one of diallyl phthalate, diallyl isophthalate and low molecular weight homopolymer thereof, diallyl terephthalate, diallyl itaconate, N,N'-diallyl tartardiamide, N,N'-diallyl melamine, diallyl adipate, diallyl succinate, diallyl sebacate, diallyl oxalate, diallyl maleate, diallyl azelate, triallyl trimellitate, triallyl citrate, and triallyl orthoformate, triallyl borate, trimethylol propane trimethacrylate, divinyl benzene and diallyl malonate.

2. The composite of Claim 1 where the rubber composition is sulfur cured with said reinforcement.

3. The composite of Claim 2 where said reinforcement is composed of at least one steel filament or cord of cabled filaments having a microscopically porous metal coating thereon composed primarily of brass and/or zinc.

4. The composite of Claim 2 where said compound is selected from at least one of diallyl phthalate, diallyl isophthalate and low molecular weight homopolymers thereof, diallyl terephthalate, diallyl itaconate, triallyl orthoformate, triallyl trimellitate and triallyl citrate.

5. The composite of Claim 2, where said steel filament has an outer, thin, practically monomolecular microporous metal coating thereon selected from at least one of zirconium, cerium, lanthanum, nickel, cobalt, tin, titanium, zinc, copper, brass and bronze plated on the steel wire.

6. The composite of Claim 4 where said steel filament is brass coated and the brass coat itself has an outer coat of zinc.

7. The composite of Claim 2 or 5 where said steel is carbon steel and the major component of said brass is alpha brass.

8. The composite of Claim 2 or 4 where said wire filament has a protective overcoat of benzotriazole.

9. The composite of Claims 2, 3, or 4 where said rubber is selected from at least one of natural rubber, synthetic cis-1,4-polyisoprene, polychloroprene, cyclene rubbers, rubbery polymers derived from 1,3-butadiene, butadiene/styrene copolymers, isoprene/styrene copolymers, epichlorohydrin homo and copolymers, butadiene/acrylonitrile copolymers, EPDM rubbers, butyl rubbers, halobutyl rubbers, norbornene rubbers, thiokol rubbers, and blends thereof.

10. A pneumatic or semi-pneumatic rubber tire having a generally toroidal shape and comprised of a general construction containing a tread, spaced inextensible beads and sidewalls connecting said beads and tread and with a supporting carcass therefor, where said carcass is a metal cord-reinforced sulfur-cured rubber composite of Claim 1.

11. The rubber tire of Claim 9 where said cord is composed of about 2 to about 50 cabled metal-plated steel filaments, said filament composed of steel filament having a microscopically porous metal coating thereon composed primarily of brass and/or zinc.

12. The tire of Claim 9 where said steel filament has an outer, thin, practically monomolecular microporous metal coating thereon selected from at least one of zirconium, cerium, lanthanum, nickel, cobalt, tin, titanium, zinc, copper, brass and bronze plated on the steel wire.

13. The tire of Claim 10 where said steel filaments have an outer coating of brass and said brass itself has an outer coat of zinc.

14. The tire of Claims 11 or 12 where said steel is carbon steel and the major component of said brass is alpha brass.

15. The tire of Claims 11 or 12 where said wire filament has a protective overcoat of benzotriazole.

16. The tire of Claims 2, 10 or 11 where said rubber is selected from at least one of natural rubber, synthetic cis-1,4-polyisoprene, polychloroprene, cyclene rubbers, rubbery polymers derived from 1,3-butadiene, butadiene/styrene copolymers, isoprene/styrene copolymers, epichlorohydrin homo and copolymers, butadiene/acrylonitrile copolymers, EPDM rubbers, butyl rubbers, halobutyl rubbers, norbornene rubber, thiokol rubbers and blends thereof with a minor portion of rubbery block copolymers selected from at least one of styrene/isoprene/styrene and styrene/butadiene/styrene block copolymers.

17. An industrial article of manufacture selected from at least one of industrial conveyor belt, power transmission belt and hose which are, at least in part, constructed of the metal cord-reinforced sulfur-vulcanized rubber composite of Claims 1, 2 or 3.

European Patent Office

EUROPEAN SEARCH REPORT

0073174

Application number

EP 82 63 0083

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	GB-A-1 449 844 (NIPPON ZEON) *Claim 7*		C 08 J 5/10 C 08 L 21/00
A	FR-A-2 120 890 (BRIDGESTONE) *Page 1* & GB - A - 1 338 930 (Cat.D)		
E,X	EP-A-0 065 476 (GOODYEAR) *Claim 1*	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			C 08 J C 08 L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	06-12-1982	VAN HUMBEECK F.W.C.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03.82

0062735
Nummer der Anmeldung

Europäisches Patentamt

EUROPÄISCHER RECHERCHENBERICHT

EP 82 10 0830.7

EINSCHLÄGIGE DOKUMENTE

Kategorie	Kennzeichnung des Dokuments mit Angabe, soweit erforderlich, der maßgeblichen Teile	betrifft Anspruch
A	DE - A1 - 2 510 219 (J. HEIDENHAIN) * Anspruch 8; Fig. 6 *	1
D,A	DE - A - 1 773 403 (J. HEIDENHAIN)	1

KLASSIFIKATION DER ANMELDUNG (Int Cl.³)

G 01 B 7/02

RECHERCHIERTE SACHGEBIETE (Int. Cl.³)

G 01 B 7/00

KATEGORIE DER GENANNTEN DOKUMENTE

X: von besonderer Bedeutung allein betrachtet
Y: von besonderer Bedeutung in Verbindung mit einer anderen Veröffentlichung derselben Kategorie
A: technologischer Hintergrund
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E: älteres Patentdokument, das jedoch erst am oder nach dem Anmeldedatum veröffentlicht worden ist
D: in der Anmeldung angeführtes Dokument
L: aus andern Gründen angeführtes Dokument

&: Mitglied der gleichen Patentfamilie, übereinstimmendes Dokument

X Der vorliegende Recherchenbericht wurde für alle Patentansprüche erstellt.

Recherchenort	Abschlußdatum der Recherche	Prüfer
Berlin	12-07-1982	KÖHN

EPA form 1503.1 06.78